

Continuous Mercury and Chloride Monitors for Coal Gasifiers

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Introduction

The capability to continuously monitor and effectively control critical effluents must be developed in order to implement new clean coal technologies. Although mercury (Hg) and hydrogen chloride (HCl) concentrations in hot, high-pressure gases from power producing systems are of environmental and technological concern, instruments suitable for determining Hg and HCl in those environments have not yet been sufficiently developed and tested. On-line analysis is more complex for such systems than for more conventional coal-based power producing systems because of the high temperatures (up to 500°C) and pressures (up to 300 psi) involved. In addition, the different gas compositions in emerging coal-based power producing systems relative to those present in conventional combustors can pose special analytical problems. Concentrations of Hg are anticipated to be in the range of 2 - 200 ppb_w in the raw gas. Concentrations of HCl are anticipated to be in the range of 50 - 500 ppm in the raw gas and less than 1 ppm after the flue gas is treated (1-3).

Objectives

Ames Laboratory will develop an integrated sampling and analysis system suitable for on-line monitoring of Hg and HCl in advanced coal-based gasifiers. The objectives of this project are to 1) summarize current technology for monitoring Hg and HCl in gaseous effluents, 2) identify analytical techniques for such determinations in high-temperature, high-pressure gases from coal-based systems for producing electrical power, 3) evaluate promising analytical approaches, and 4) produce reliable on-line monitors which are adaptable to plant-scale diagnostics and process control.

Project Description

Commercially available instruments which were potentially suitable for monitoring Hg and HCl in coal gasifiers were screened and the most promising techniques were selected for laboratory evaluation. For Hg, the techniques selected for further consideration were atomic absorption (AA) and atomic fluorescence (AF). For HCl, gas-filter-correlation infrared spectroscopy (GFCIR), a dry colorimetric procedure, and ion mobility spectroscopy (IMS) were selected for testing in the laboratory. The analytical systems selected for use in on-line Hg and HCl

analyzers will be adapted for application to monitoring hot pressurized gases from coal gasifiers. Additional work will involve developing suitable gas conditioning and sample introduction systems. That work may be as important as the development of the analytical detectors themselves. After the laboratory studies have been completed, prototype instruments will be tested and evaluated in the field.

Results

Mercury Studies. In previous work (4), we performed a laboratory evaluation of two Hg detectors (one each based on AA and AF). After carefully considering the pros and cons of each approach, AA was selected as the method of choice for monitoring Hg in coal gasifier streams. The decision was based largely on the fact that sample gases could not be passed directly into the AF detection cell because of severe quenching of the fluorescence signal by gases present in coal gasification streams. The quenching effects would result in inadequate detection limits for the anticipated Hg levels if the sample gases were passed directly into the detection cell.

In recent work, recoveries of Hg injected into simulated gasifier streams were studied. Injections of Hg were initially made into stainless steel lines containing the simulated gasifier streams as the gases were slowly heated to 200°C. When the gas stream contained a mixture of CO, CO₂, CH₄, COS, H₂, and H₂S, no Hg was recovered in the temperature range studied. In follow-up tests, Hg injections were made into Teflon sample lines containing various gas mixtures. Full recoveries were obtained when the carrier gas contained mixtures of only H₂, CO, CO₂, and CH₄, while recoveries decreased to about 75% when the carrier gas also contained either 1% (v/v) H₂S or 0.5% COS. Because the majority of the Hg was recovered using the simulated gasifier streams in Teflon lines, even in the presence of sulfur-containing gases, chemical interactions between Hg and the other gases present are not believed to be the primary cause of poor Hg recoveries observed using the same gas mixtures in stainless steel sample lines. Rather, the low recoveries in steel appear to be from wall losses. Although these problems may be alleviated by the use of continuous Hg streams (as opposed to injections), which allow for conditioning of the walls of the sample lines, the results from the Hg injections are being used to identify potential areas of concern regarding sampling of Hg in coal gasifiers.

Potential spectral interferences were studied with our AA detector (Thermo Separation Products, Model 3200) for confirmation of published absorbance values, as a check on equipment calibration, and to provide useful information related to the deuterium (D₂) lamp background correction approach that is being investigated. Tests were performed by using injections of various gas species and by using continuous streams of the gases of interest directly into the AA detector. For the injections, 100 µL of a given gas were injected into an air or nitrogen stream flowing at a rate of 170 cc/min into the detector. For the continuous flows of potentially interfering gases, diluted streams of each gas were examined. By blending 10 cc/min of a given gas with the carrier gas stream flowing at 1000 cc/min, a 1% concentration for each gas of interest was obtained. Gases tested include CH₄, CO₂, CO, COS, H₂S, SO₂, O₂, and H₂. The SO₂ and O₂ were included since some of the gas conditioning approaches being considered involve oxidation of the gas stream.

For the injections, comparable results were obtained for both air and nitrogen carrier gases. Relative absorbance values based on the injections of individual gases were in agreement with those obtained using the continuous flows of potentially interfering gases. For the tests using continuous flows of the gases of interest, experimental absorbance readings were in good agreement with published values. Not surprisingly, results from the injections and continuous gas streams indicated that the strongest interferences were for the sulfur-containing gases. The absorbance produced by COS was comparable to that produced by H₂S, although H₂S is of much greater concern because it will be present in gasifier streams at much higher concentrations than COS. By using published absorptivity values and our own experimental data, we determined that about 500 ppm_v H₂S will produce a signal equivalent in magnitude to the signal from a 1 ppb_w Hg stream. Based on the anticipated H₂S levels in coal gasification effluents, the interference from H₂S could produce an absorption value equivalent to that observed for a 10 ppb_w Hg stream. This interference is severe enough that either background corrections must be made or else the H₂S must be eliminated before the sample gas enters the detection cell. Although the H₂S could be oxidized, this would produce SO₂, which interferes 30 times more strongly than H₂S.

In addition to the interferences from COS, H₂S and SO₂, a substantial absorbance was noted when CO was introduced to the AA cell. This is of concern since gasifier streams contain large concentrations of CO. From our review of published work thus far, it is somewhat surprising that CO would be an interfering gas. Also, injections of "pure" CO obtained from two different manufacturers gave absorbance values that differed by more than a factor of two. Therefore, additional work will be performed to determine whether the interference is actually from CO or whether it is from some impurity in the CO gas stream.

The possibility of using a commercially available AA instrument with a D₂ lamp background correction was investigated. Based on data provided by several major manufacturers of those instruments, blank readings had too much base line variability for determining Hg in gasifier streams at the anticipated Hg concentrations. However, due to the high stability of our AA detector, we explored the possibility of adding a D₂ lamp to our AA detection system. As a step in investigating the potential for using a D₂ lamp background correction approach, the AA base line variation was observed by directing the detector towards an external D₂ lamp while the AA cell in our instrument was removed. The magnitude of base line noise using the D₂ lamp was typically about 10 times greater than when using the Hg lamp built into the unit. By using the base line variabilities observed with our Hg lamp and with a D₂ lamp in our laboratories, relative errors of about 10% and 80% at Hg concentrations of 10 and 1 ppb_w, respectively, are anticipated. The magnitude of these errors resulting from the use of a D₂ lamp is acceptable at the levels of Hg involved. It should also be emphasized that these measured base line variabilities pertain to a specific D₂ lamp, and it may be possible to purchase a D₂ lamp that is even more stable than the one we currently have. Dual photodiodes were also purchased and subsequently tested to determine whether they would be suitable for use in conjunction with a D₂ lamp for background correction of the Hg signal. Experimental results indicate that the use of the photodiodes should not add significant analytical uncertainties in the determination of Hg at the ppb level.

In addition to using a D₂ lamp for a background correction, we also considered the possibility of using a D₂ lamp for both the background correction and source lamp for the Hg determination. However, after performing a variety of tests, it appears that the resolution necessary for the determination would be too large for the sensitivity required.

One manufacturer of AA systems performed some tests to observe the base line stability obtained using an electrodeless discharge lamp (EDL) in their attempt to reduce base line noise levels from that observed using a Hg hollow cathode lamp. Although the base line using an EDL was less noisy than that obtained with a Hg hollow cathode lamp, there was still too much base line variability for our monitoring application. Our AA detector has about an order of magnitude less base line variability than the commercially available AA unit using an EDL.

Hydrogen Chloride Studies. In previous work (4), a Thermo Environmental Instruments Model 15 Gas Filter Correlation IR (GFCIR) HCl analyzer was evaluated in our laboratories. When using compressed gases for the HCl standard, instrument readings were very stable, baseline fluctuations were minimal, and the calibration curve was linear in the range of about 25 to 3000 ppm_v HCl. Erratic responses were noted at lower concentrations, which could be from uncertainties in blending the calibration gases. When HCl permeation tubes were used to provide gas stream concentrations of HCl from 0.2 to 2 ppm_v, the instrument response showed good linearity from about 0.5 to 2 ppm_v. Long equilibration times and pronounced memory effects were noted when passing low concentrations of HCl through the sample lines and flow meters. Other tests indicated that 300-400 ppm CH₄ (a known interference) gives a response equivalent to 1 ppm HCl. Depending on the relative concentrations of CH₄ and HCl in the gasifier effluents, 75% to nearly 100% of the CH₄ will need to be removed prior to HCl determinations. Results of recent work are discussed below.

Colorimetric Method. Testing and evaluation of an MDA Scientific Model 7100 Continuous Gas Analyzer was performed. That instrument is based on exposing a strip of color-indicating paper to a metered sample stream. Any HCl present in the sample gas reacts with the paper to form a colored, circular (i.e., "dot") stain. The intensity of the stain is proportional to the HCl concentration and is quantified by using a photocell to detect the amount of reflected light from the portion of the paper exposed to the sample gas. The color-indicating paper is in the form of a continuous strip and is mounted in a cassette cartridge, which is referred to as a chemcassette. This allows the monitor to provide "continuous" analysis of a gas stream. The standard chemcassette determines HCl in the range of about 0.2 - 50 ppm_v. In addition, a low-level chemcassette is available for determining HCl down to about 50 ppb_v. The low-level chemcassette employs different reaction chemistry than the standard chemcassette and requires different instrument software. Our tests were performed using both the standard and low-level tapes.

The manufacturer recommends humidifying the sample stream to 25-75% relative humidity (RH) at ambient temperature. Significant errors can result if the RH is outside of this range. If dry gases are to be used, a special low-RH calibration should be performed. The instrument

manufacturer reports that HCN and HF are possible interferences, but little information was available on the magnitude of those interferences. Both of those gases are expected to be present in coal gasifier streams. We investigated the HF interference by using anhydrous HF from a permeation tube with room air as the carrier gas. The HCN interference was studied by using a compressed gas cylinder containing 1% HCN in a nitrogen balance. Compressed gas cylinders containing HCl in a nitrogen balance were used for the tests with the standard chemcassette, while permeation tubes containing aqueous HCl were used for the tests with the low-level chemcassette. Results obtained with the standard and low-level HCl chemcassettes are discussed separately below. Relative standard deviations (RSDs) for all tests were typically $\pm 5\%$ or less.

Standard Chemcassettes. A calibration curve was obtained by blending 100 ppm HCl (in a nitrogen balance) with air and passing the blended gases into the analyzer. These results are shown in Figure 1. The measured detection limit was on the order of several tenths of a ppm and the calibration curve was generally linear down to several ppm. At lower concentrations, the nonlinearity may be a result of instrument inaccuracies or dilution errors in the gas stream. When 25 ppm HCl in nitrogen was sent to the detector, results were about 50% higher when the gas stream was humidified. Although it was known that results could be affected by the relative humidity of the gas, these results demonstrate that the errors incurred can be substantial.

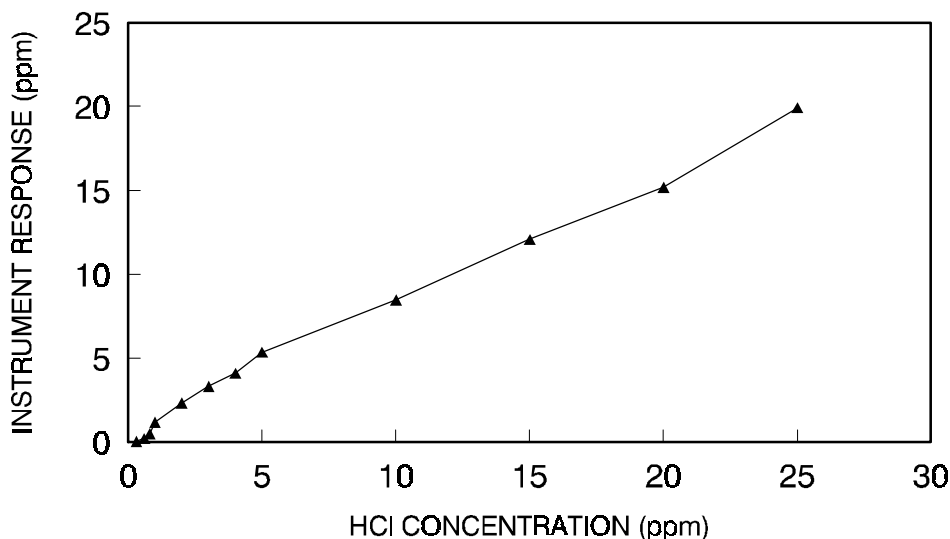


Figure 1. Calibration Curve Obtained with the Colorimetric Analyzer Using Blended Gases.

When 15 ppm dry HF in air was sent to the HCl analyzer in the absence of HCl, a reading corresponding to about 0.5 ppm HCl was obtained. When those gases were humidified by passing the diluent air over a pool of water prior to blending with the HF stream, the reading on the HCl analyzer dropped to zero. The signal quickly returned to 0.5 ppm once the source of added humidity was removed. The elevated humidity appeared to suppress the signal due to HF

and is probably related to the chemcassette tape chemistry. For tests with HF in the presence of HCl, 15 ppm HF (the anticipated maximum concentration in gasifier effluents) in a 1 ppm HCl stream had a negligible effect on the reported HCl concentration, regardless of whether the gas stream entering the analyzer was humidified.

When 100 to 2000 ppm HCN was sent to the analyzer in the absence of HCl, a small positive response on the analyzer was noted. The ratio of the HCN concentration to the instrument response was generally constant, with 1000 ppm HCN giving a reading corresponding to about 1 ppm HCl. As was the case with HF, the signal went to zero when humidity was added by humidifying the diluent air prior to blending it with the HCN stream. In gas streams containing 10 ppm HCl, the HCl signal was not significantly affected by the presence of 150 ppm HCN.

Low-Level Chemcassettes. With the low-level chemcassette, the measured detection limit was on the order of 50 ppb HCl. As the HCl concentration was decreased from 400 to 75 ppb, good linearity in the calibration curve was obtained. However, as the HCl concentration decreased further, some anomalous readings indicative of desorption wall effects were observed. The permeation tube was removed from the chamber, but significant HCl concentrations were still reported by the analyzer for more than two days when air passing through the chamber was sent to the calibrator. When the calibrator was set to send zero air to the analyzer, the HCl analyzer consistently reported "0 ppb". Since the gases from the calibrator passed through common sample lines in each case, and since the gas flow rate through the sample line was the same for each set of tests, the memory effects are likely to be within the calibrator itself rather than in the analyzer or sample transport lines. After ensuring that no HCl was being emitted from the calibrator, a calibration curve was obtained by increasing the HCl concentration (HCl concentration was decreased in the initial tests). Because of pronounced adsorption/desorption effects, the slopes and intercepts of the two calibration curves (one each from increasing and decreasing the HCl concentration) were much different. This has important implications regarding field monitoring and calibration of analytical instruments, since wall effects can result in lengthy equilibration times (e.g., 24 hours or more).

Humidification of the nitrogen stream containing HCl had a more pronounced effect on the HCl reading when using the low-level chemcassette as opposed to the standard chemcassette. However, this is not necessarily due to differences in tape chemistry between the standard and low-level chemcassettes. The humidity may have provided a "flushing" effect which removed adsorbed HCl in the sample lines. Such a flushing effect could be much more prominent (greater percent change in concentration reading) at the relatively low HCl concentrations used with the low-level chemcassettes.

HF was a major interference when using the low-level chemcassette. When the gas stream entering the analyzer contained 1000 ppb of HF only (i.e., no HCl), an HCl reading of 130 ppb was obtained. In contrast to the standard chemcassette where humidifying the gas stream eliminated the signal observed when using HF only, the opposite effect was observed with the low-level tape. For example, when the gases were humidified, the reading increased from 130 ppb to nearly 200 ppb. These results demonstrate the potential magnitude of the HF interference and also indicate that HF from the permeation tube was getting to the analyzer after

humidifying the gas stream. Thus, 15 ppm HF (the anticipated maximum concentration in gasifier streams) could cause a signal equivalent to that produced from several ppm HCl. Therefore, the HF interference should be negligible if the HCl concentration is significantly greater than the HF concentration. If the HCl concentrations are 1 ppm or greater, it would be preferable to use the standard chemcassette since HF interferences with that chemcassette are less prominent.

When 2800 ppm HCN was introduced to the analyzer in the absence of HCl, a signal equivalent to only 100 ppb HCl was obtained, indicating that HCN is not a significant interference with the low-level chemcassette in low-humidity gases. When the tests were repeated in the presence of 150 ppb HCl, the HCN again had little effect on the HCl reading. Results on the effects of humidity and on the effects of HCN in humidified gases were inconclusive in view of data uncertainties. Those uncertainties may be related to severe adsorption/desorption effects, "flushing" of the walls in the presence of humidity, or chemical interactions occurring on the detection tape or sample transport lines.

Discussion. Unlike other monitors being considered, the colorimetric analyzer provides visual confirmation of results through the use of colored dots. This is useful at low HCl readings where, for other instruments, it can be difficult to distinguish between a small HCl reading from a baseline variation. Also, by simply replacing a chemcassette, the colorimetric monitor (with the appropriate internal calibrations and software) can be used to monitor other individual gas species of interest. Another potential advantage to the colorimetric monitor is the smaller amount of internal surface area, where adsorption/desorption phenomena can lead to memory effects.

Disadvantages of the colorimetric monitor include the sensitivity of the technique to relative humidity of the sample gases, the need for different chemcassettes employing different chemistry for different ranges of HCl concentrations, and possible complications regarding color formation in the complex gas matrices of a coal gasifier. If methane can be effectively removed from sample gases without affecting HCl concentrations, using the colorimetric monitor with the standard chemcassette does not appear to offer any significant advantages over the gas-filter-correlation infrared (GFCIR) unit we investigated previously. Although the low-level chemcassette can detect lower levels of HCl than GFCIR, our results suggest that data should be viewed with extreme caution when using that chemcassette in complex gas matrices. In view of these considerations, the dry colorimetric analyzer will not be employed for on-line analysis of coal gasifier streams.

Ion Mobility Spectroscopy. Ion mobility spectroscopy (IMS) was evaluated in our laboratories using an IMS unit manufactured by ETG. As with the colorimetric method, IMS has a narrow dynamic range (about 200). For our initial tests, a concentration range of 0.1 to 20 ppm_v was used. Gases with higher concentrations of HCl can still be analyzed by diluting the gas stream. Compressed gases were used to examine instrument response and the linearity of calibration curves. Air was blended with a 100 ppm HCl gas stream (in a nitrogen balance) to give the desired HCl concentrations. When the HCl flow was first sent to the detector, it took about 20 minutes to reach 90% of its final response to the HCl stream. However, after this initial period

in which HCl was equilibrating with the walls of the sample transport lines and portions of the IMS system, the unit responded rapidly to changes in HCl concentration. The detector gave a linear response to HCl concentrations ranging from 1 to 25 ppm, as shown in Figure 2. The discrepancy between the HCl reading on the instrument and our nominal HCl concentrations may reflect gas metering uncertainties or insufficient conditioning periods in our work. Those possibilities will be explored further. Additional tests with the IMS system are in progress to examine potential interferences and to examine instrument response to HCl concentrations in the ppb range.

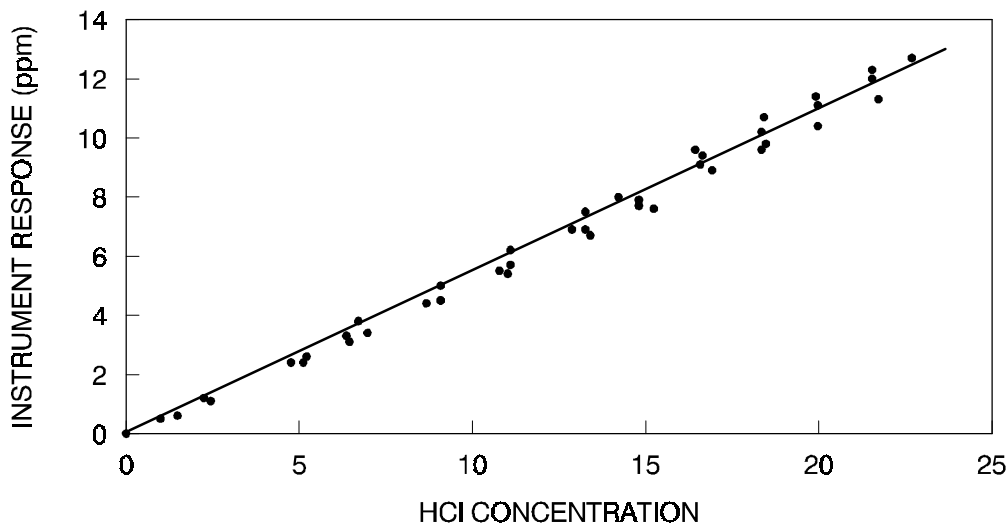


Figure 2. Calibration Curve Obtained for IMS Unit Using Blended Gases.

Ammonia Removal. In the presence of ammonia (NH_3), chloride losses can occur during sample transport due to formation and deposition of solid NH_4Cl . This compound can be kept in the vapor phase during sample transport by heating the sample lines. However, since most of the HCl monitors being considered operate at relatively low temperatures (less than 100°C) and require the chloride to be present as HCl rather than NH_4Cl , the presence of NH_3 gases in the sample stream presents a problem. Consequently, it is desirable to remove the NH_3 from the gasifier stream in order to avoid the formation of NH_4Cl prior to determining HCl.

Tests were performed with a beaded (1/8-inch) platinum catalyst (United Catalysts, Louisville, KY) on an alumina substrate to determine how effectively it removes NH_3 gases. For these tests 3% (v/v) NH_3 in a given carrier gas stream was passed through about 100 cc of catalyst with a total gas flow of about 1 liter/minute. The temperature of the catalyst was varied from ambient to 400°C , and a given temperature was maintained to within 5°C for 30 minutes before obtaining semiquantitative measurements of the NH_3 concentration exiting the catalyst tube using color-indicating paper sensitive to NH_3 . In base line tests using blends of nitrogen and NH_3 , little or no NH_3 was removed as the temperature was increased to 400°C . When the NH_3

was blended with air rather than nitrogen, virtually no NH_3 was removed at temperatures below about 250°C . As the temperature was increased to about 250°C , exothermic reactions began occurring, which made it more difficult to maintain the desired temperature. Also, the formation of water was evident (condensation was observed after exiting the catalyst tube) and no NH_3 was detected with the color-indicating paper. After heating the catalyst tube outlet to avoid condensed water, a Sensidyne pump and color-indicating tubes (accurate to within 25%) were used to help quantify the NH_3 concentration exiting the catalyst tube at 300°C . Results indicated that the NH_3 concentration was less than 1 ppm_v, which equates to a NH_3 removal efficiency of 100%.

The water formed during the catalytic oxidation of NH_3 was very acidic ($\text{pH} < 1$) and is believed to be nitric acid. When the catalyst tube was at 300°C and the outlet of the tube was heated to avoid condensation, gases exiting the tube were bubbled into deionized water for several minutes. Analysis of this water sample by ion chromatography indicated that it had a lot of nitrate and a considerable amount of an unidentified compound, which is believed to be a nitric acid precursor. Nitric acid is often commercially made by the catalytic oxidation of NH_3 using the Ostwald process. In that process, NH_3 is oxidized to produce NO and H_2O . The NO is subsequently oxidized to NO_2 , which then dissolves in water to form HNO_3 and NO . Attempts were made to maintain the oxidation of NH_3 without promoting the subsequent formation of nitric acid by initially activating the catalyst at about 250°C and then subsequently decreasing the temperature. As the temperature was gradually decreased, it was held at each desired temperature for periods ranging from 2 to 12 hours. The NH_3 was completely removed and acidic water was noted regardless of temperature. This was true even after 12 hours at 60°C , which was the minimum temperature attained with no external heat supplied to the catalyst. The catalytic oxidation reactions were disrupted only after terminating the NH_3 flow and purging the catalyst tube with either air or nitrogen. After doing so, the catalyst tube was heated to 200°C and the NH_3 flow was resumed. No NH_3 removal was observed and no moisture was formed even after 7 hours at that temperature. Apparently, a minimum activation energy is required in order to initiate the catalytic oxidation of NH_3 . Also, these results indicate that lowering the reaction temperature after initial activation of the catalyst is not a viable approach for preventing acid formation when 3% NH_3 is in an air stream. Attempts are currently being made to destroy the NH_3 without forming nitric acid by using air/nitrogen blends to decrease the oxygen content of the gas stream. In doing so, it may be possible to have sufficient oxygen for oxidizing the NH_3 , but not for subsequent oxidation of the NO byproduct to NO_2 .

Hydrocarbon Removal. Because methane is a severe interference in the determination of HCl by the IR method, tests were performed to determine whether a platinum/palladium catalytic converter can effectively remove hydrocarbon gases at reasonably low temperatures. Preliminary tests were performed by passing an air stream containing approximately 10% propane by volume through an automotive catalytic converter. At the time of these tests, the commercially available platinum catalyst used for the NH_3 studies was not yet available. Semiquantitative results indicated that hydrocarbon gases could largely be destroyed by the converter at temperatures of less than 500°C . Tests were also performed to see whether the converter could pass low concentrations of HCl . For those tests, HCl from a compressed gas

cylinder was diluted to 25 ppm and then passed through the catalytic converter at various temperatures. The gases exiting the converter were analyzed using a dry colorimetric analyzer. Little or no HCl was detected at the converter outlet until the temperature reached 450°C or more, where substantial amounts of HCl were emitted. This suggests that it may be possible to use platinum catalysts to destroy hydrocarbons without affecting the HCl content. Additional tests are being performed using the platinum catalyst from United Catalysts.

Future Activities

For Hg, problems associated with the use of AA will be investigated. The primary problem anticipated is the presence of interfering compounds (e.g., aromatic hydrocarbons and sulfur compounds) in actual gasifier streams. Future work will focus on studying approaches for either removing interfering compounds through gas conditioning or for performing suitable spectral background corrections during analysis of the gasifier streams. The best approach for use in an on-line analyzer for coal gasifiers will then be selected. Because of the possibility that oxidized Hg species (e.g., dimethyl Hg) may be present in gasifier streams, work will be performed with a pyrolyzer intended for use in the on-line monitor to ensure that it is pyrolyzing oxidized Hg species to elemental Hg (required for detection) with essentially 100% conversion efficiencies.

For HCl, the analytical method to be used for the on-line monitor will be selected. Studies on the delivery of known amounts of HCl will continue. The use and accuracy of permeation tubes and permeation tube calibration systems will continue to be investigated. Methods for removing or destroying NH₃ and hydrocarbons in the sample gas prior to HCl analysis will continue to be tested.

For both Hg and HCl, subsequent testing will include determining the effects of gas composition (including moisture content) on detection limits, precision, and accuracy. The effects of sample line material will also be considered. Modifications to existing commercial instruments will be made in order to adapt those systems for use with gasifier streams.

Suitable sample handling systems will be developed. Gas conditioning steps which will be required include temperature and pressure adjustments, filtering particulate matter, and removing interfering gases. The removal of moisture from gas streams without affecting the analyte will also be studied. The amount and type of gas conditioning will be largely dependent on the analytical methodology employed. The effects of any necessary sample conditioning steps (e.g., moisture removal) on analyte concentrations will be examined. Ultimately, prototype integrated analytical systems which appear to be acceptable based on results of laboratory studies will be tested in the field.

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